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Analysis of Spatial and Temporal Distribution of
Inhaleable Air Particulates in Ontario

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Abstract:

Source identification of airborne particulate matter is possible using a wide range of analytical techniques which can, in principle, supply the trace element and isotope distribution in specific particles. We have found that the kinetics of the conversion of sulphite ions to sulphate ions in solutions in contact with particulate matter is useful both as a means of source identification and as an indicator of the chemistry of a given air mass. The reactivity of the material can be combined with conventional analytical methods can be used in conjunction with spatial and temporal distribution data for source identification.

Introduction:

A wide range of sophisticated analytical techniques are available for the analysis of airborne particulate matter. In principle these yield information which should be useful in the identification of specific particulate sources. For instance, a given sample might be expected to contain a unique set of trace elements which could be further characterized according to their oxidation state and chemical environment (1) - (i.e. oxide or pure metal) and/or the isotope distribution of individual elements (2), which is often site-specific. Finally the reactivity of the particulate matter as a catalyst for specific atmospheric reactions is a potentially important indicator of their source. Accordingly we have obtained a bulk analysis of filter material using SIMS, ICP/MS, ICP/AES, XRF and SEM, in addition XPS, XRD, EM, and SAM have been combined with these techniques to establish the distribution and oxidation states of the various elements detected. These results have shown a ready distinction between material, principally clays, resulting from surface wind erosion and those from high temperature combustion dominated by iron oxides and fused alumino-silicate material. Mobile sources can be identified by the presence of significant amounts of amorphous carbon in conjunction with Br (3) from free radical scavengers in the fuel and, till recently, lead (4). Evidence suggests that the trace element distribution in the alumino-silicate material may be indicative of the origin of the sample while the nature and quantity of amorphous carbon is probably from inefficient combustion as in low temperature fires and poorly tuned diesel engines. Given ideal conditions credible source identification should be possible using complimentary results from this equipment, however, each instrument carries a unique set of problems. For instance SIMS is capable of detecting virtually all the elements and their isotopes but is a semi-quantitative technique, XPS while supplying the oxidation state of each element is sensitive only to surface atoms and is plagued by problems associated with charging of the sample. Application of the techniques is also time consuming and expensive. Chemical reactivity can be measured relatively rapidly and easily by using ion chromatography to monitor the rate of conversion of sulfite ion to sulfate ion in solutions in contact with air particulates. The results can be used to select particle assemblies showing unusual reactivity for further analysis, thus reducing the number of samples that receive intensive

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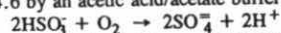
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study and the kinetics observed may be used to indicate the most likely catalytic agents, which are in turn often site-specific

Experimental:

The air sampling was carried out by the Ontario Ministry of the Environment using high volume sampling (Ca 1200 Litres per minute) for a twenty-four hour period at selected sites throughout Ontario using a high purity quartz filters. The collection equipment was so designed that the particles collected had an aerodynamic diameter of 10 microns and smaller.

The catalytic activity of the filters was measured by cutting a planchette having an area of 5 cm² from the centre of the loaded filter. This was then immersed in a solution 20 ppm in HSO₃⁻ at a pH maintained at 4.6 by an acetic acid/acetate buffer. The kinetics of the reaction:



were monitored at room temperature using a Dionex DX-100 Ion Chromatograph. [SO₄²⁻] in solution prior to the addition of the HSO₃⁻ were used as an indicator of total loading on the filter. XRF data was used to estimate the concentration of various elements on the filter surface while ICP/AES and FAAS were used to monitor the concentrations of selected ions in solution with special attention to Fe, both because it is abundant on the filter material and Fe³⁺ is an important catalyst in the conversion of HSO₃⁻ to SO₄²⁻ (5).

Model systems were used to establish the kinetics to be expected from a series of standard materials which were suspected catalysts. Thus the catalytic activity of various clays, supplied by the Geology Department of the University of Western Ontario, metallic iron, iron oxide, goethite (FeO.OH) and Fe³⁺, and that of pure graphite and graphite oxidized with H₂O₂ for 12 hours were studied.

Results and Discussion:

Figure 1 shows the reactivities of a large number of filters taken from different sites. The reactivity varies widely between individual samples. This confirms our hypothesis that the chemical reactivity, measured in this way can be used to identify filter material of special interest for further study. Figure 2 shows the variation in the reactivity of filters versus their total particulate loading as measured by the total sulfate present on the filter. No correlation is evident. This is an important result showing that the differences in reactivity observed between filters do not simply represent variable filter loading. Figure 3 shows the variation of reactivity with time at a single collection site. No clear pattern is evident. This is hardly surprising since weather conditions i.e. wind speed and direction, snow cover and precipitation will be important determinants of the amount and nature of the material collected. Those results show that it is possible to select a relatively small number of filters having high reactivity from very large set. The selection will not be biased toward heavily loaded filters nor will filters from specific sites be used unless weather conditions are favourable.

Carbon from various sources is often an important component in the particulate matter. Its catalytic effects vary widely as a function of surface area, physical form (i.e. graphite or amorphous carbon), and degree of oxidation.(6) In our work high purity graphite yielded a specific rate constant of $1.94 \times 10^{-3} \text{ min}^{-1}$ on oxidation with H₂O₂ this value increased to 1.59

$\times 10^{-2} \text{ min}^{-1}$ for the catalytic conversion of sulfite to sulfate assumed to be first order in sulfite.(7) Carbon can be removed from filters by low temperature ashing. Filters showing high reactivity can be subjected to this procedure, if the resulting material no longer shows catalytic activity then carbon is responsible and further analysis of the surface area and functional group distribution on the carbon should be undertaken.

Metals are also important catalysts.(8) XRF shows the most abundant transition metal on the filters to be iron. Studies with model systems show that iron metal, Fe₂O₃ and FeO.OH are not catalysts while Fe³⁺ is. Figure 4 shows the reactivity as a function of the concentration of Fe³⁺ in solution in a model system while Figure 5 shows the reactivity of the system as a function of Fe³⁺ in contact with the filters. This latter figure shows a good correlation between [Fe³⁺] and reactivity, but approximately 25% of the data points are anomalous. The anomalous data points indicate that either an inhibitor or second catalyst may be present in the filter material. Figure 6 shows the individual filter reactivity versus iron coverage as determined by XRF. Failure to achieve a good correlation is evidence for the presence of iron in relatively insoluble form which implies Fe in clay and/or Fe₂O₃ from smelting operations.

Finally clay minerals have been identified as catalysts and thus high reactivity may often result from clay minerals. The rare earth content of the clays may well be site specific. In addition our results show that the activity of illite clays is inhibited by phosphate ion. The mechanism of inhibition and the probable relationship to phosphate fertilizer and to agricultural activity is currently under investigation.

Conclusions:

The wide range of analytical equipment currently available should, in principle, allow source identification of specific air particulates using element and isotope distribution in conjunction with the chemical form and reactivity of the sample. The wide range of measurements required are however difficult, time consuming and expensive, as well failures are always possible because of the inherently small sample size.

Catalysis by material trapped on high volume filters can be studied relatively easily using IC to measure the kinetics of the conversion of sulfite to sulfate. So far we have identified three major catalytic systems: amorphous carbon, aluminosilicate minerals (clays) and metal ions (principally Fe³⁺). Filters showing high reactivity may be selected for further, detailed analysis. In any event, considerable information indicative of the source can be obtained from the sulfite/sulfate reaction kinetics, for instance oxidized amorphous carbon appears to be more reactive than pure material. The former results from low temperature oxidation. Our studies on carbon reactivity are at an early stage and the literature indicates that our own limited results are not conclusive and that this area is poorly understood. The usefulness of the carbon for source identification remains problematic. Clay minerals, when present in their unaltered form contain site specific trace elements. Altered clay minerals (spherical glasses) are evidence of high temperature combustion. The suite of unreactive iron is indicative of iron in clays or iron oxides while Fe³⁺ is probably from metallic iron and is indicative of smelting or ore processing operations.

Kinetic measurements of the kind described here yield significant information about the nature

of the particulate matter on individual filters. These results combined with detailed surface and chemical analysis are good indicators of the origin of specific sample material.

Glossary:

EM	Electron Microprobe
FAAS	Flame Atomic Absorption Spectroscopy
IC	Ion Chromatography
ICP/MS	Inductively Coupled Plasma/Mass Spectrometry
ICP/AES	Inductively Coupled Plasma/Atomic Emission Spectroscopy
SAM	Scanning Auger Spectroscopy
SEM	Scanning Electron Microscopy
SEM/EDX	Scanning Electron Microscopy/Energy Dispersive X-Ray Analysis
SIMS	Secondary Ion Mass Spectrometry
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

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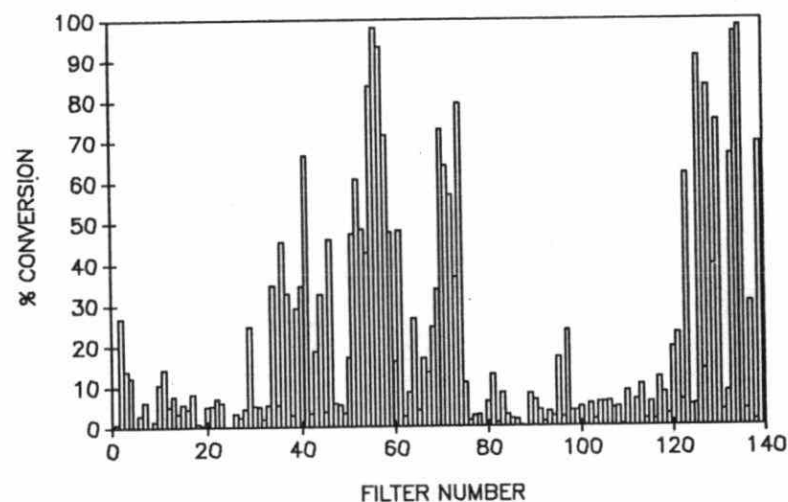


Figure 1. % Conversion for the catalytic oxidation of S(IV) to S(VI) showing the variation in reactivity for filters from different sites.

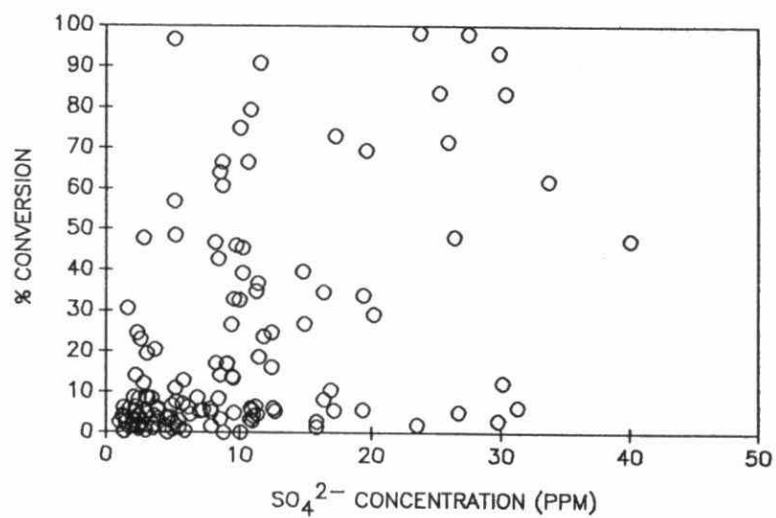


Figure 2. % Conversion versus SO_4^{2-} concentration on filters.

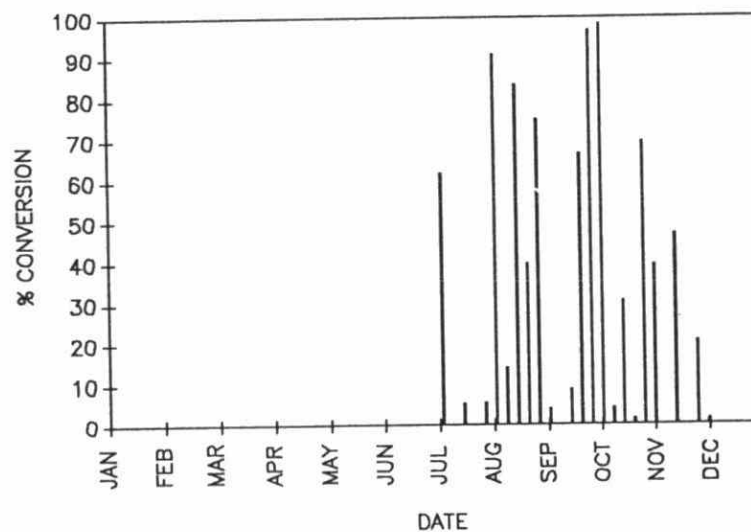


Figure 3. % Conversion for station 71342 as a temporal distribution.

(Note: PM_{10} sample collection started July 3, 1989.)

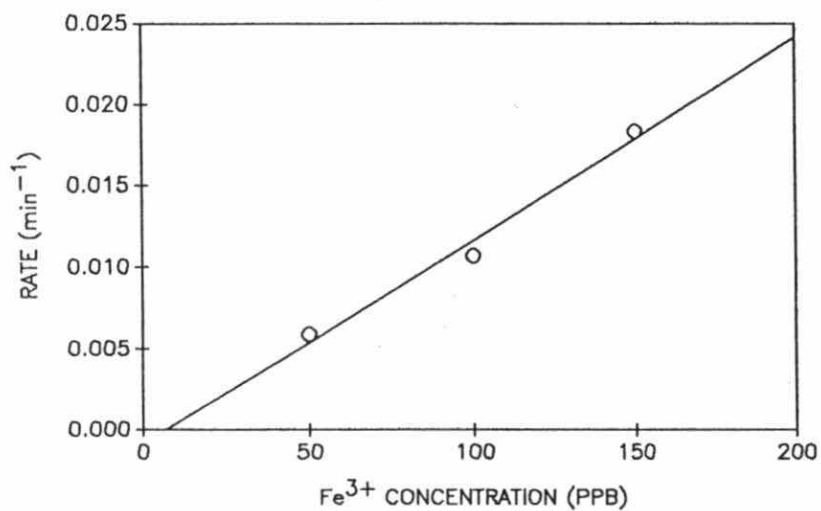


Figure 4. Rate constant versus Fe³⁺ concentration in model system for the catalytic oxidation of S(IV) to S(VI) at pH 4.7.

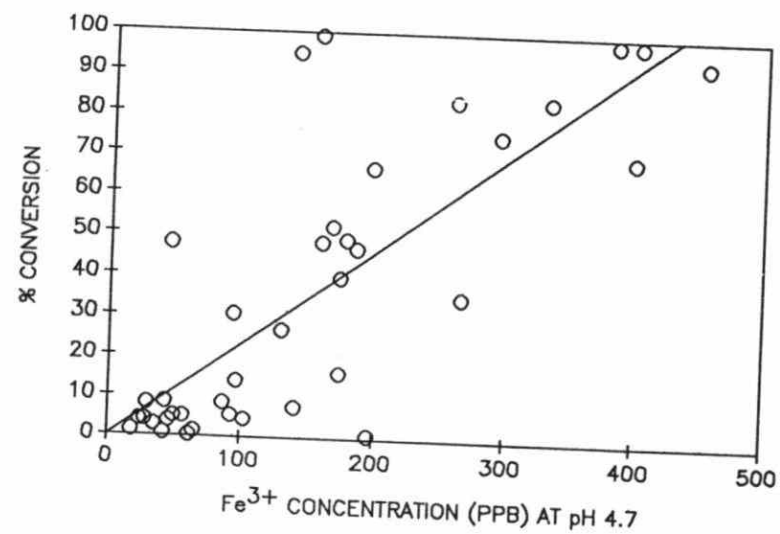


Figure 5. % Conversion versus Fe³⁺ concentration of filters at pH 4.7 for the catalytic oxidation of S(IV) to S(VI).

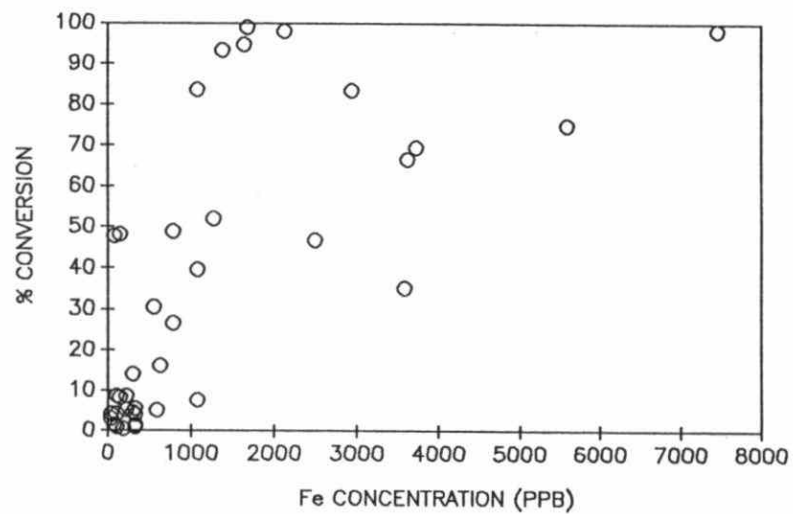


Figure 6. % Conversion versus Fe concentration as measured by XRF (Ontario Ministry of the Environment).

(Note: $\mu\text{g}/\text{m}^3$ converted to our units (ppb) by conversion factor 1 $\mu\text{g}/\text{m}^3$ equal to 37.27 ppb.)



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